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(54) Polycarbonate polyol and coating composition based thereon

Polycarbonatpolyol und darauf basierende Beschichtungsmischung

Polyol de polycarbonate et composition de revêtement à base de celui-ci

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EP 0 562 577 B1

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Description

The present invention relates to a coating composition containing a polycarbonate polyol.

5 Polyols are widely used for paint, adhesive or elastomer in combination with a curing agent which reacts with hydroxyl group. The polyols generally include polyether polyol such as polypropylene glycol and polytetramethylene glycol; polyester polyol obtained by reacting polyvalent carboxylic acid and polyhydric alcohol; polylactone polyol obtained by reacting lactone with alcohol; poly(meth)acrylate polyol obtained by polymerizing (meth)acrylate having a hydroxyl group such as 2-hydroxyethyl methacrylate. They are selectively used for various applications according to the required performances.

10 However, since the polyether polyol has ether bonds, the paint film obtained by using it has a poor heat stability and weather stability. Since polyester polyol and polylactone polyol have ester bonds, the paint film obtained from them is inferior in water resistance. Further, poly(meth)acrylate polyol has good weather stability but it is being poor in dynamic property.

15 In order to obtain the paint film free from such drawbacks, it is proposed to use a polycarbonate polyol having a carbonate bond in its molecular structure. For example, Japanese Kokai Publication 45522/1990 discloses a coating composition which comprises (1) a polycarbonate polyol obtained from a saturated aliphatic α,ω -glycol having 4 to 12 carbon atoms and tri-(hydroxyethyl)-isocyanurate and (2) a melamine resin or isocyanate curing agent.

20 However, since the saturated α,ω -glycol has a high crystallinity, the obtained polycarbonate polyol has crystallinity. Consequently, this paint composition has a poor solubility in usual solvents and a poor compatibility with the curing agent. The inferior compatibility with curing agent causes a poor curing ability and poor appearance of the paint film, and results in the decline of durability and physical property of the paint film.

25 US-A-4,533,729 discloses a process for preparing specified amorphous polycarbonate polyols. A branched chain polyhydric alcohol and a straight chain polyhydric alcohol are used. A preferred branched chain polyhydric alcohol is neopentylglycol and a preferred straight chain polyhydric alcohol is 1,6-hexanediol. A mixture of neopentylglycol and pentaerythritol may also be used.

DE-A-19 21 866 discloses the use of one branched diol having a specific formula with one polyol being selected from 1,1,1-trimethylolpropane and pentaerythritol. The branched diol may be neopentylglycol.

30 The object of the invention is to provide a coating composition which has a good solubility in a solvent, a high compatibility with a curing agent; a preferred heat and water resistance and dynamic property and preferred physical property such as adhesive ability to other paint film and durability.

In order to solve this problem a coating composition is provided which is as defined in claim 1. Preferred features are described in the sub-claims 2 to 7.

The present invention also provides a polycarbonate polyol which is very suitable for the above coating composition, as defined in claim 8.

35 The polyfunctional polycarbonate polyol contained in the coating composition of the present invention is obtained by reacting known polyhydric alcohols with a carbonyl component selected from the group consisting of phosgene, a chloroformate, a dialkylcarbonate, a diarylcarbonate, an alkylene carbonate and a mixture thereof. The process for producing the polycarbonate polyol is known, for example from U.S. Patents 3,689,462 and 4,533,729.

40 The polyfunctional polycarbonate polyol has at least 2, preferably at least 3 hydroxyl group in one molecule. The number of hydroxyl groups is counted in average. The use of a polycarbonate wherein the average hydroxyl group number is less than two is undesirable because of the decrease of the crosslinking ability and the decrease of the durability of the coated film.

45 The polycarbonate polyol has a number average molecular weight of 400 to 10,000, preferably 1,000 to 5,000. When the number average molecular weight is smaller than the above range, stickiness or softness remains in the cured film and thus the physical properties of the coated film become inferior. If the number average molecular weight is larger than the above range, the viscosity of the polycarbonate polyol becomes too high and as the result the coating ability and smoothness of the paint film are deteriorated.

50 The polycarbonate polyol has a hydroxyl value of 50 to 350, preferably 100 to 310. When the hydroxyl value is less than the above range, the crosslinking ability becomes too low and the durability of the coated film decreases, while if it is larger than the above range, the crosslinking ability becomes too high and the coated film becomes rigid and its physical properties deteriorate.

55 The polyhydric alcohol used in the present invention for preparation of the polyfunctional polycarbonate polyol is a mixture essentially consisting of 10 to 90 mol %, preferably at least 25 mol % of the specified branched diols, 10 to 90 mol %, preferably 13 mol % of the specified tri- or higher-hydric alcohols.

The tri- or higher-hydric alcohol is more preferably a 4-6 hydric alcohol.

By using the alcohol component which contains the branched diols, an amorphous polycarbonate polyol is obtained and as the result compatibility of the coating composition improves. By using the alcohol component which contains tri- or higher hydric alcohol, the hydroxyl value of the resulting polycarbonate polyol increases and thus curing property

of the coated film improves.

When the content of the branched diols is less than 10 mol%, the resulting polyfunctional polycarbonate polyol crystallizes and its solvent solubility and compatibility with melamine resin is deteriorated. When the content of tri- or higher hydric alcohol is less than 10 mol%, functional group number of the resulting polycarbonate polyol decreases and sufficient curing property is not obtainable.

When the tri- or higher hydric alcohol is a sugaralcohol, they have optical isomers, all (D-isomer, L-isomer and DL-isomer) of which can be used for the present invention.

The balance of the polyhydric alcohol component can be the other polyhydric alcohols, for example straight chain diols such as 1,3-propylene glycol, 1,4-butane diol, 1,5-pentane diol, 1,6-hexane diol, 1,8-octane diol, 1,9-nonane diol and 1,10-decane diol.

The polyfunctional polycarbonate polyol used in the present invention may have a carboxyl group with an acid value of less than 50. Where the coating composition does not contain any curing catalyst for the melamine resin, such as p-toluenesulfonic acid or an alkyl-substituted naphthalenesulfonic acid, it is impossible to obtain a sufficiently cured film. Therefore it is preferred to use the polycarbonate polyol having carboxyl groups with an acid value of less than 50.

When acid value is larger than 50, curing property is excellent but a large amount of carboxyl group remains in the cured film and therefore the water resistance of the film remarkably deteriorates.

The polycarbonate polyol containing such carboxyl groups is obtained by reacting the polycarbonate polyol with an acid anhydride or a dicarboxylic acid at 120-180 °C. The acid anhydride may be phthalic anhydride, trimellitic anhydride, tetrahydro-phthalic anhydride, succinic anhydride and itaconic anhydride and the dicarboxylic acid may be adipic acid, sebatic acid, phthalic acid or isophthalic acid.

The polycarbonate polyol of the present invention preferably has a carbonate portion (i.e. -O-CO-O-) of 20 to 40 % by weight, more preferably 22 to 34 % by weight, by controlling the amount of the carbonyl component and the polyhydric alcohol component. If the content of the carbonate portion is less than 20 % by weight, the cured film is soft and adhesiveness of the film also reduces. If it is more than 40 % by weight, the polycarbonate polyol is too viscous and the resulting coated film has poor smoothness and very stiff.

The melamine resin used for the curing agent of the present invention may be the resin obtained by addition-condensation of an amine compound such as melamine, guanamine and urea with formaldehyde by art-known method or the resin obtained by further addition-condensation of such resin with alcohol. For instance, it may be methylated melamine, butylated melamine, methylated benzoguanamine or butylated benzoguanamine.

A portion of the melamine resin, preferably 0 to 50 % by weight of the melamine resin, can be replaced with an isocyanate compound. Examples of the isocyanate compounds are tolylene diisocyanate, diphenylmethane diisocyanate, xylylene diisocyanate, hexamethylene diisocyanate, isophorone diisocyanate, biuret thereof, isocyanurate thereof or a trimethylopropane-adduct thereof.

The solid weight ratio of polycarbonate polyol (1) / melamine resin (2) is preferably within the range of 90/10 to 50/50. When the ratio of polycarbonate polyol and melamine resin is larger than the aforesaid range, a sufficient curing property is not obtained, while if it is smaller than the above, the crosslinking ability becomes too high, the coated film becomes too hard and physical properties of the coated film such as adhesive ability deteriorates.

The coating composition of the present invention may contain various polyols, various pigments, organic solvents, curing catalyst and various additives, if necessary.

Examples of the polyol are polyethers such as polypropylene glycol, polytetramethylene glycol; polyester polyols derived from polyhydric carboxylic acid and polyhydric alcohol; polylactone polyol obtained by the reaction of lactone and alcohol; poly(meth)acrylate polyol obtained by polymerization of (meth)acrylate containing a hydroxyl group.

The pigment useful for the coating composition of the present invention may be titanium oxide, silica, carbon black, molybdenum orange, copper phthalocyanine or quinacridone red,

The curing catalyst may be p-toluenesulfonic acid, xylenesulfonic acid, dodecylbenzenesulfonic acid, didodecyl-naphthalenesulfonic acid, didodecyl-naphthalenesulfonic acid, dinonylnaphthalenesulfonic acid, dinonylnaphthalene-disulfonic acid, their amine blocks or phosphoric acid.

In the present invention, an organic solvent may be used to adjust the viscosity of the coating composition to the condition preferred for coating workability. The concrete examples of such organic solvent may be xylene, toluene, ethyl acetate, butyl acetate, methyl ethyl ketone and methyl isobutyl ketone. These solvents are preferably used in the amount where solid content of paint becomes about 30-70 wt%.

Other additives may be surface active agent, antioxidant, UV ray absorbing agent, pigment dispersing agent or fluidity adjusting agent,

The present invention is illustrated by the following Examples.

Preparation Example 1

In a glass reactor vessel equipped with stirrer, thermometer and fractionating column, 1,000 wt parts (4.7 mol) of

5 diphenyl carbonate, 232 wt parts (1.5 mol) of 2-methyl-1,8-octanediol, 432 wt parts (2.7 mol) of 1,9-norane diol and 259 wt parts (1.0 mol) of trimethylolpropane dimer were mixed and the mixture was heated to 185 °C in nitrogen gas stream. While fractionating phenol from the reaction mixture, it was gradually heated to 220 °C and when most of phenol was fractionated, the residual phenol was completely removed under vacuum of 5-10 mmHg. As the result, a liquid polycarbonate polyol (I) with hydroxyl group number of 147 was obtained. Number average molecular weight of gel permeation chromatography (GPC) was 2,360 and average hydroxyl group number was 6.2.

Preparation Example 2

10 In a glass reactor vessel equipped with stirrer, thermometer and fractionation column, 1,000 wt parts (11.1 mol) of dimethyl carbonate, 650 wt parts (5.5 mol) of 3-methyl-1,5-pentanediol and 1 wt part of tetraisopropyl titanate as catalyst were mixed and under normal pressure, the mixture was heated at 100 °C for 5 hours and thereafter the temperature was raised to 200 °C taking 5 hours and methanol produced by the reaction of dimethyl carbonate was fractionated.

15 After the end of fractionation of methanol, the mixture was reacted for 2 hrs. under reduced pressure, the produced methanol and excess dimethyl carbonate were thus fractionated and the reaction product was obtained. Proton NMR analysis of the reaction product indicated that it had methyl carbonate terminal and number average molecular weight by GPC was 6,840. When 99 wt parts (0.40 mol) of trimethylol propane dimer was added to 500 wt parts of thus obtained reaction product, and ester exchange reaction was conducted for 4 hrs. at 200 °C, polycarbonate polyol (II) with hydroxyl group number of 154 was obtained. Number average molecular weight measured by GPC was 2,350 20 and average hydroxyl group number in one molecule was 6.5.

Preparation Example 3-9

25 Polycarbonate polyol (III)-(IX) was prepared in the same way as in Preparation Example 1 except that the composition ratio shown in Table 1 below was used. Table 2 indicates the mol ratio of the composition of its alcohol component and Table 3 indicates the characteristics of polycarbonate polyol obtained.

Preparation Example 10

30 36 weight parts of phthalic acid anhydride was added to 500 weight parts of polycarbonate polyol (I) obtained in Example 1 and the reaction was continued for 2 hrs. at 180 °C and polycarbonate polyol (X) with hydroxyl group number of 120 and acid value of 27 was obtained. Number average molecular weight measured by GPC was 2,580 and average hydroxyl group number in one molecule was 5.5. Table 2 shows the mol ratio of the composition of alcohol component 35 and Table 3 shows the characteristics of polycarbonate polyol obtained.

Preparation Example 11

40 86 wt parts of phthalic acid anhydride was added to 500 wt parts of polycarbonate polyol (IV) obtained in Preparation Example 3 and the reaction was continued for 2 hrs. at 180 °C and polycarbonate polyol (XI) with hydroxyl group number of 112 and acid value of 61 was obtained. Number average molecular weight measured by GPC was 2,400 and average hydroxyl group number in one molecule was 4.8. Table 2 shows the mol ratio of the composition of its alcohol component and Table 3 shows the characteristics of polycarbonate polyol obtained.

Preparation Example 12

45 Polycarbonate polyol (XII) with hydroxyl group number of 105 was obtained in the same way as in Preparation Example 1, using 1,000 wt parts (4.7 mol) of diphenyl carbonate, 520 wt parts (4.4 mol) of 1,6-hexane diol and 365 wt parts (1.4 mol) of tris-hydroxyethyl isocyanurate. Number average molecular weight measured by GPC was 2,710 and average hydroxyl group number in one molecule was 5.1. Table 2 shows the mol ratio of the composition of its alcohol 50 component and Table 3 shows the characteristics of polycarbonate polyol obtained.

Table 1 Formulation of Preparation Examples 3-9 (Wt parts)

Preparation Ex. No.	Polycarbonate polyol No.	DPC ¹	3MPD ²	2MPD ³	BEPD ⁴	CHMP ⁵	HD ⁶	ND ⁷	D-TMP ⁸	TMP ⁹
3	III	1,000	520	-	-	-	-	-	259	-
4	IV	1,000	393	-	-	-	-	-	500	-
5	V	1,000	-	370	-	-	-	-	230	46
6	VI	1,000	-	-	467	128	-	-	225	-
7	VII	1,000	-	-	-	-	1,109	-	-	-
8	VIII	1,000	-	-	-	-	-	747	-	134
9	IX	1,000	322	-	-	-	-	-	751	-

Table 2 Mol ratio of alcohol component in polycarbonate polyol

Preparation Ex. No.	Polycarbonate polyol No.	Mol % of alcohol component		
1	I	Branched diols MOD:10.28.8	Strait chain diols ND:51.9	Tri- or higher alcohols D-TMP:19.3
2	II	3MPD:89.4	-	D-TMP:10.6
3	III	3MPD:81.5	-	D-TMP:18.5
4	IV	3MPD:62.3	-	D-TMP:37.7
5	V	2MPD:76.5	-	D-TMP:17.2 TMP:6.3
6	VI	BEPD:62.0 CHDM:18.8	-	D-TMP:19.2
7	VII	-	HD:100.0	-
8	VIII	-	ND:98.4	TMP:1.6
9	IX	MPD:48.2	-	D-TMP:51.8
10	X	MOD:28.8	ND:51.9	D-TMP:19.3
11	XI	MPD:81.5	-	D-TMP:18.5
12	XII	-	HD:75.8	THEI:24.2

Table 3 Characteristics of polycarbonate polyol

Preparation Ex. No.	Polycarbonate polyol	Molecular weight (Mn(GPC))	Hydroxyl value (mgKOH/g)	Acid value (mgKOH/g)	Number of Hydroxyl groups	Appearance
1	I	2360	147	-	6.2	Light yellow liquid
2	II	2350	154	-	6.4	Light yellow liquid
3	III	2030	193	-	7.0	Light yellow liquid
4	IV	1500	310	-	8.3	Light yellow liquid
5	V	1940	159	-	5.5	Light yellow liquid
6	VI	2400	122	-	5.2	Light yellow liquid
7	VII	350	320	-	2.0	White solid
8	VIII	11300	15	-	3.0	White solid
9	IX	1250	388	-	8.6	Light yellow liquid
10	X	2580	120	2.7	5.5	Light yellow liquid
11	XI	2400	112	61	4.8	Light yellow liquid
12	XII	2710	105	-	5.1	Yellow solid

Symbols in Tables 1-3 respectively represent following compounds:

5	DPC:	Diphenyl carbonate
	3MPD:	3-Methyl-1,5-pentane diol
	2MPD:	2-Methyl-1,3-propane diol
	BEPD:	2-Butyl-2-ethyl-1,3-propane diol
10	CHDM:	1,4 -Cyclohexanedimethanol
	HD:	1,6-Hexane diol
	ND:	1,9-Nonane diol
	D-TMP:	Dimer of trimethylolpropane
	TMP:	Trimethylolpropane
15	MOD:	2-Methyl-1,8-octane diol
	THEI:	Trishydroxyethyl isocyanurate

Preparation Example 13

15 In a glass reactor vessel equipped with stirrer, thermometer and fractionation column, 1,000 wt parts (11.1mol) of dimethyl carbonate, 495 wt parts of 2-methyl-1,3-propanediol and 1 wt part of tetraisopropyl titanate as catalyst were mixed and under normal pressure, the mixture was heated at 100 °C for 5 hours and thereafter the temperature was raised to 200 °C taking 5 hours and methanol produced by the reaction of dimethyl carbonate was fractionated.

20 After the end of fractionation of methanol, the mixture was reacted for 2 hrs. under reduced pressure, the produced methanol and excess dimethyl carbonate were thus fractionated and the reaction product was obtained. Proton NMR analysis of the reaction product indicated that it had methyl carbonate terminal and number average molecular weight by GPC was 9,840. When 314 wt parts of trimethylol propane dimer was added to 500 wt parts of thus obtained reaction product, and ester exchange reaction was conducted for 4 hrs. at 200 °C to obtain a light yellow liquid polycarbonate polyol (XIII) with hydroxyl value of 189. Number average molecular weight measured by GPC was 1,940 and average hydroxyl group number in one molecule was 6.5. The resulting polycarbonate polyol XIII had a carbonate portion of 33.4 % by weight and the other portion of 66.6 % by weight.

Preparation Example 14

30 A polycarbonate polyol (XIV) was prepared as generally described in Preparation Example 13, with exception that 886 wt parts of 2-butyl-2-ethyl-1,3-propane diol was employ in stead of 2-methyl-1,3-propane diol and 250 wt parts of trimethylol propane dimer was employed. The resulting polycarbonate polyol XIV had a molecular weight of 2,400 and a hydroxyl value of 122, and average hydroxyl group number in one molecule was 5.2. It also had a carbonate portion of 25.5 % by weight and the other portion of 74.5 % by weight.

Preparation Example 15

40 A polycarbonate polyol (XV) was prepared as generally described in Preparation Example 13, with exception that 254 wt parts of pentaerythritol dimer was employed instead of trimethylol propane dimer and 650 wt parts of 3-methyl-1,5-pentane diol was employed instead of 2-methyl1,3-propane diol. The resulting polycarbonate polyol XV had a molecular weight of 2,300 and a hydroxyl value of 245, and average hydroxyl group number in one molecule was 10.0. It also had a carbonate portion of 30.9 % by weight and the other portion of 69.1 % by weight.

Preparation Example 16

45 A polycarbonate polyol (XVI) was prepared as generally described in Preparation Example 13, with exception that 183 wt parts of sorbitol was employed instead of trimethylol propane dimer. The resulting polycarbonate polyol XIV had a molecular weight of 2,150 and a hydroxyl value of 250, and averay hydroxyl group number in one molecule was 9.6. It also had a carbonate portion of 32.3 % by weight and the other portion of 67.7 % by weight.

Example 1

50 70 wt parts of polycarbonate polyol (I) obtained in the Preparation Example I, 50 wt parts of butylated melamine resin (Yuban 128 having a solid content of 60 % by weight, manufactured by Mitsui Toatsu Chemical Co.) and 1 wt part of para-toluene sulfonic acid curing catalyst were mixed under stirring and the mixture was coated on a steel panel for the thickness of 60 μ and baked for 25 minutes at 140 °C to obtain the cured film. Characteristics of the obtained paint and the cured film were evaluated as to the following items. The results are shown in Table 4.

Method of evaluation of the performance of paint and the coated film.

Property of paint: State of mixing of the paint was evaluated visually.

Smoothness: Smoothness of the cured film was evaluated visually.

Curing property: Curing condition of the coated film was evaluated by the stickiness of film checked by finger touch.

5 Solvent resistance: The coated film was rubbed by gauze soaked with xylene for 50 reciprocating rounds and defects of the coated film was evaluated visually.

Impact resistance: DuPont test: 1/2 φ x 500 g x 30 cm

Water resistance: The coated film was immersed in water at 40 °C for 480 hrs., the coated film was given scar in grating form (100 squares of 1 mm/mm), an adhesive tape was applied on it and the tape was peeled off. Water resistance was indicated by the number of grating squares left on the surface.

Example 2-6

15 Cured film was obtained, in the same way as in Example 1 except that polycarbonate polyol (II)-(VI) obtained in the Preparation Example 2-6 were respectively used instead of polycarbonate polyol (I). Various characteristics of the obtained paint and the cured film were evaluated. The results are shown in Table 4.

Example 7

20 70 wt parts of polycarbonate polyol (X) obtained in the Preparation Example 10 and 50 wt parts of butylated melamine resin (Yuban 128, manufactured by Mitsui Toatsu Chemical Co.) were mixed under stirring and the mixture was coated on a steel panel for the thickness of 60 µ and baked at 140 °C for 25 minutes to obtain the cured the coated film. Various characteristics of the obtained paint and the cured film were evaluated. The results are shown in Table 4.

25 Examples 6 to 9

30 70 wt parts of polycarbonate polyol (XIII) to (XV) obtained in Preparation Example 13-15; 30 wt parts of butylated melamine resin (Yuban 128, manufactured by Mitsui Toatsu Chemical Co.) and 1 wt part of p-toluenesulfonic acid curing catalyst were mixed under stirring and the mixture was coated on a steel panel for the thickness of 60 µ and baked for 25 minutes at 140 °C to obtain a cured film. Characteristics of the obtained paint and the cured film were evaluated, and the results are shown in Table 4.

Example 11

35 70 wt parts of polycarbonate polyol (XVI) obtained in Preparation Example 16, 30 wt parts of butylated melamine resin (Yuban 128, manufactured by Mitsui Toatsu Chemical Co.), 1 wt part of p-toluenesulfonic acid curing agent and 16 wt parts of an isocyanurate of hexamethylene diisocyanate (available from Nippon Polyurethane K.K. as Colonate EX: NCO equivalent = 197, solid content = 75 wt %) were mixed under stirring and the mixture was coated on a steel panel at a thickness of 60 µ and baked at 140 °C for 25 minutes to obtain a cured film. The same evaluations were 40 conducted and the results are shown in Table 4.

Comparative Example 1 and 2

45 Cured the coated film was obtained in the same way as in Example 1 except that polycarbonate polyol (VII)-(VIII) obtained in Preparation Example 7-8 were used and xylene was used as solvent for the amount that the solid contents occupy 70 wt% of the total. Various characteristics of thus obtained paint and cured the coated film were evaluated. The results are shown in Table 4.

Comparative example 3

50 Cured the coated film was obtained in the same way as in Example 1 except that polycarbonate polyol (IX) obtained in the Preparation Example 9 was used instead of polycarbonate polyol (I). Various characteristics of thus obtained cured the coated film were evaluated. The results are shown in Table 4.

55 Comparative example 4

Cured the coated film was obtained in the same way as in Example 1 except that polycarbonate polyol (XI) obtained in Preparation Example 11 was used instead of polycarbonate polyol (I). Various characteristics of thus obtained paint

EP 0 562 577 B1

and cured the coated film were evaluated. The results are shown in Table 4.

Comparative example 5

- 5 Cured the coated film was obtained in the same way as in Example 1 except that polycarbonate polyol (XII) obtained in Preparation Example 12 was used instead of polycarbonate polyol (I). Various characteristics of thus obtained paint and the coated film were evaluated. The results are shown in Table 4.

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Table 4 Evaluation of cured film

Ex. No.	Polycarbonate No.	Appearance	Smoothness	Curing ability	Solvent resistance	Impact resistance	Water resistance
1	I	Clear	Smooth	Good	Good	Good	100/100
2	II	Clear	Smooth	Good	Good	Good	100/100
3	III	Clear	Smooth	Good	Good	Good	100/100
4	IV	Clear	Smooth	Good	Good	Good	100/100
5	V	Clear	Smooth	Good	Good	Good	100/100
6	VI	Clear	Smooth	Good	Good	Good	100/100
7	X	Clear	Smooth	Good	Good	Good	100/100
8	XIII	Clear	Smooth	Good	Good	Good	100/100
9	XIV	Clear	Smooth	Good	Good	Good	100/100
10	XV	Clear	Smooth	Good	Good	Good	100/100
11	XVI	Clear	Smooth	Good	Good	Good	100/100
Comp. Ex. 1	VII	Cloudy	Smooth	Poor	Dissolved	-	0/100
Comp. Ex. 2	VIII	Paste	Round	Fairly good	Swelled	Good	80/100
Comp. Ex. 3	IX	Clear	Smooth	Good	Good	Cracks	100/100
Comp. Ex. 4	XI	Clear	Smooth	Good	Good	Good	0/100
Comp. Ex. 5	XII	Cloudy	Round	Good	Swelled	Cracks	85/100

Claims

1. A coating composition comprising:
 - 5 (1) a polycarbonate polyol having a number average molecular weight of 400-10000 and a hydroxyl value of 50-350, and
 - (2) a melamine resin curing agent,

10 wherein polyhydric alcohols constituting said polycarbonate polyol essentially consist of 10 to 90 mol-% of branched diols selected from the group consisting of 3-methyl-1,5-pentanediol, 2-methyl-1,3-propanediol, 1,4-cyclohexanedimethanol and 2-methyl-1,8-octanediol, and 10 to 90 mol-% of tri- or higher hydric alcohols, selected from the group consisting of glycerin, trimethylolethane, trimethylolpropane, trimethylol propane dimer, 1,2,7,8-octane tetraol, ribitol, arabitol, xylitol, sorbitol, allitol, mannitol, dulcitol, pentaerythritol dimer and mixtures thereof, and a ratio of component (1)/component (2) is within the range of 90/10-50/50 based on solid weight.

- 2. The coating composition according to claim 1 wherein said polycarbonate polyol is prepared by reacting said polyhydric alcohols with a carbonyl component selected from the group consisting of phosgene, a chloroformate, a dialkylcarbonate, a diarylcarbonate, an alkylene carbonate and a mixture thereof.
- 20 3. The coating composition according to claim 1 wherein said polycarbonate polyol has at least 2 hydroxyl groups in one molecule.
- 4. The coating composition according to claim 1 wherein said tri- or higher hydric alcohol is a 4-6 hydric alcohol.
- 25 5. The coating composition according to claim 1 wherein said polyfunctional polycarbonate polyol has carboxyl group with less than 50 acid value.
- 6. The coating composition according to claim 1 wherein said polycarbonate polyol has a carbonate portion of 20 to 40 % by weight.
- 30 7. The coating composition according to claim 1 wherein a portion of said melamine resin is replaced with an isocyanate compound in an amount of up to 50 wt.-%.
- 8. A polycarbonate polyol having a number average molecular weight of 400 to 10000, a hydroxyl value of 50 to 350 and a carbonate portion represented by (-O-CO-O-) in an amount of 20 to 40 % by weight, prepared by reacting:
 - 40 (a) a carbonyl component selected from the group consisting of phosgene, a chloroformate, a dialkylcarbonate, a diarylcarbonate, an alkylene carbonate and a mixture thereof,
 - (b) a polyhydric alcohol component essentially consisting of 10 to 90 mol-% of branched diols, selected from the group consisting of 3-methyl-1,5-pentanediol, 2-methyl-1,3-propanediol, 1,4-cyclohexanedimethanol and 2-methyl-1,8-octanediol, and 10 to 90 mol-% of tri- or higher hydric alcohols selected from the group consisting of glycerin, trimethylolethane, trimethylolpropane, trimethylolpropane dimer, 1,2,7,8-octane tetraol, ribitol, arabitol, xylitol, sorbitol, allitol, mannitol, dulcitol, pentaerythritol dimer and mixtures thereof.
- 45 9. The polycarbonate polyol according to claim 8 wherein said polycarbonate polyol has a carboxyl group with less than 50 acid value.

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Patentansprüche

1. Beschichtungszusammensetzung, umfassend:
 - 55 (1) ein Polycarbonatpolyol mit einem Molekulargewicht im Zahlenmittel von 400 bis 10.000 und einem Hydroxylwert von 50 bis 350, und
 - (2) ein Melaminharz-Härtungsmittel,

wobei mehrwertige Alkohole, die einen Bestandteil des genannten Polycarbonatpolyols bilden, im wesentlichen aus 10 bis 90 mol-% verzweigten Diolen, ausgewählt aus der Gruppe bestehend aus 3-Methyl-1,5-pentandiol, 2-Methyl-1,3-propandiol, 1,4-Cyclohexandimethanol und 2-Methyl-1,8-octandiol, und 10 bis 90 mol-% drei- oder höherwertigen Alkoholen, ausgewählt aus der Gruppe bestehend aus Glycerin, Trimethylolethan, Trimethylolpropan, Trimethylolpropandimer, 1,2,7,8-Octantetraol, Ribitol, Arabitol, Xylitol, Sorbitol, Allitol, Mannitol, Dulcitol, Pentaerythritoldimer und Mischungen davon, bestehen, und das Verhältnis von Komponente (1) zu Komponente (2) in dem Bereich 90:10 bis 50:50, basierend auf dem Feststoffgewicht, liegt.

2. Beschichtzungszusammensetzung gemäss Anspruch 1, wobei das genannte Polycarbonatpolyol durch Umsetzung des genannten mehrwertigen Alkohols mit einer Carbonylkomponente, ausgewählt aus der Gruppe bestehend aus Phosgen, Chlorformiat, Dialkylcarbonat, Diarylcarbonat, Alkylencarbonat und einer Mischung davon, hergestellt wird.
3. Beschichtzungszusammensetzung gemäss Anspruch 1, wobei das genannte Polycarbonatpolyol mindestens zwei Hydroxylgruppen in einem Molekül hat.
4. Beschichtzungszusammensetzung gemäss Anspruch 1, wobei der genannte drei- oder höherwertige Alkohol ein vier- bis sechswertiger Alkohol ist.
5. Beschichtzungszusammensetzung gemäss Anspruch 1, wobei das genannte polyfunktionelle Polycarbonatpolyol Carboxylgruppen mit einem Säurewert von weniger als 50 hat.
6. Beschichtzungszusammensetzung gemäss Anspruch 1, wobei das genannte Polycarbonatpolyol einen Carbonatanteil von 20 bis 40 Gew.% hat.
7. Beschichtzungszusammensetzung gemäss Anspruch 1, wobei ein Anteil des genannten Melaminharzes durch eine Isocyanatverbindung in einer Menge von bis zu 50 Gew.% ersetzt wird.
8. Polycarbonatpolyol mit einem Molekulargewicht im Zahlenmittel von 400 bis 10.000, einem Hydroxylwert von 50 bis 350 und einem Carbonatanteil, dargestellt durch (-O-CO-O-) in einer Menge von 20 bis 40 Gew.%, hergestellt durch die Umsetzung:
 - (a) einer Carbonylkomponente, ausgewählt aus der Gruppe bestehend aus Phosgen, Chlorformiat, Dialkylcarbonat, Diarylcarbonat, Alkylencarbonat und einer Mischung davon,
 - (b) einer mehrwertigen Alkoholkomponente, im wesentlichen bestehend aus 10 bis 90 mol-% eines verzweigten Diols, ausgewählt aus der Gruppe bestehend aus 3-Methyl-1,5-pentandiol, 2-Methyl-1,3-propandiol, 1,4-Cyclohexandimethanol und 2-Methyl-1,8-octandiol, und 10 bis 90 mol-% eines drei- oder höherwertigen Alkohols, ausgewählt aus der Gruppe bestehend aus Glycerin, Trimethylolethan, Trimethylolpropan, Trimethylolpropandimer, 1,2,7,8-Octantetraol, Ribitol, Arabitol, Xylitol, Sorbitol, Allitol, Mannitol, Dulcitol, Pentaerythritoldimer und Mischungen davon.
9. Polycarbonatpolyol gemäss Anspruch 8, wobei das genannte Polycarbonatpolyol eine Carboxylgruppe mit einem Säurewert von weniger als 50 hat.

Revendications

1. Composition de revêtement comprenant:
 - (1) un polycarbonate-polyol présentant un poids moléculaire moyen en nombre de 400 à 10000 et un indice hydroxyle de 50 à 350, et
 - (2) un agent de durcissement en résine de mélamine,
- 55 dans laquelle les alcools polyhydroxyliques constituant ledit polycarbonate-polyol sont essentiellement constitués de 10 à 90% en mole de diols ramifiés choisis dans le groupe constitué du 3-méthyl-1,5-pentanediol, du 2-méthyl-1,3-propanediol, du 1,4-cyclohexanediol et du 2-méthyl-1,8-octanediol, et de 10 à 90% en mole d'alcools trihydroxyliques ou supérieurs, choisis dans le groupe constitué de la glycérine, du triméthyloléthane, du

triméthylolpropane, d'un dimère de triméthylol propane, du 1,2,7,8-octane tétraol, du ribitol, de l'arabitol, du xylitol, du sorbitol, de l'allitol, du mannitol, du dulcitol, d'un dimère de pentaérytritol et de mélanges de ceux-ci, et un rapport entre le composant (1) et le composant (2) se situe dans la plage de 90/10 à 50/50, calculés sur le poids de solides.

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2. Composition de revêtement selon la revendication 1, dans laquelle ledit polycarbonate-polyol est préparé en faisant réagir lesdits alcools polyhydroxyliques avec un composant carbonylé choisi dans le groupe constitué du phosgène, d'un chloroformate, d'un dialkylcarbonate, d'un diarylcarbonate, d'un carbonate d'alkylène et d'un mélange de ceux-ci.
- 10 3. Composition de revêtement selon la revendication 1, dans laquelle ledit polycarbonate-polyol présente au moins 2 groupes hydroxyle dans une molécule.
- 15 4. Composition de revêtement selon la revendication 1, dans laquelle ledit alcool trihydroxylique ou supérieur est un alcool 4-6 hydroxylique.
5. Composition de revêtement selon la revendication 1, dans laquelle ledit polycarbonate-polyol polyfonctionnel présente un groupe carboxyle présentant un indice d'acide inférieur à 50.
- 20 6. Composition de revêtement selon la revendication 1, dans laquelle ledit polycarbonate-polyol présente une partie carbonate de 20 à 40% en poids.
7. Composition de revêtement selon la revendication 1, dans laquelle une partie de ladite résine mélamine est remplacée par un composé isocyanate, en quantité pouvant atteindre 50% en poids.
- 25 8. Polycarbonate-polyol présentant un poids moléculaire moyen en nombre de 400 à 10000, un indice hydroxyle de 50 à 350 et une partie carbonate représentée par (-O-CO-O-) en quantité de 20 à 40% en poids, préparé en faisant réagir:
 - 30 (a) un composant carbonylé choisi dans le groupe constitué du phosgène, d'un chloroformate, d'un dialkylcarbonate, d'un diarylcarbonate, d'un carbonate d'alkylène et d'un mélange de ceux-ci,
 - (b) un composant alcool polyhydroxylique constitué essentiellement de 10 à 90% en mole de diols ramifiés, choisis dans le groupe constitué du 3-méthyl-1,5-pentanediol, du 2-méthyl-1,3-propanediol, du 1,4-cyclohexanediol et du 2-méthyl-1,8-octanediol, et de 10 à 90% en mole d'alcools trihydroxyliques ou supérieurs,
 - 35 choisis dans le groupe constitué de la glycérine, du triméthyloléthane, du triméthylolpropane, d'un dimère de triméthylolpropane, du 1,2,7,8-octane tétraol, du ribitol, de l'arabitol, du xylitol, du sorbitol, de l'allitol, du mannitol, du dulcitol, d'un dimère de pentaérythritol et de mélanges de ceux-ci.
- 40 9. Polycarbonate-polyol selon la revendication 8, dans lequel ledit polycarbonate-polyol présente un groupe carboxyle présentant un indice d'acide inférieur à 50.

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